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Changes in Dielectric Relaxation of Wood by Heat Treatment*¹

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Introduction

A dielectric relaxation is found in the contour diagram of the dielectric loss in a wide range of temperature and frequency for wood in the absolutely dry condition¹⁾. Dielectric measurements on wood constituents showed that the relaxation was observed in cellulose, mannan and lignin which have methylol groups, while it is not observed in xylan which does not have methylol groups²⁾. The relaxation of cellulose was absolutely eliminated by tritylation in which trityl groups are selectively introduced at primary hydroxyl groups^{3,4)}. The relaxation magnitude of cellulose was increased by decrystallization⁴⁾. These facts clarified that the relaxation of wood was due to methylol groups in the non-crystalline region.

This paper investigated changes in the dielectric relaxation due to methylol groups of wood in the absolutely dry condition by heat treatment.

Materials and Methods

Sugi (*Cryptomeria japonica*) heart wood was used. The dimension of specimens was 5 cm (*L*) × 1 cm (*R*) × 1 cm (*T*). The specimens placed in a glass container were heated using an electric oven. Treatment temperatures (*T*_{HT}) were 200, 250, 270, 300, 400, 500, 600°C and 700°C. Temperature was raised with 4°C/min up to the prescribed temperature, then kept for one hour and followed by cooling. Nitrogen gas was poured into the glass container during heating. The untreated and treated specimens were ground to powders using a Wiley mill. The powders passed a 100-mesh screen were used for the samples of dielectric measurements.

The LCR-meter (Japan Hewlett-Packard Co. Ltd., 4284A), the electrode (Ando Electric Co. Ltd., SE-30, effective diameter: 16.9 mm) equipped with a Teflon holder for powder samples and the oil bath (Ando Electric Co. Ltd., TO-3) were used for dielectric measurements. Dielectric losses (ϵ'') of the samples in the absolutely dry condition were measured at 31 frequencies between 1 kHz and 1 MHz in the temperature range from -150°C to 0°C (at intervals of 5°C). Measured values were adjusted to those at a density of 1g/cm³.

Results and Discussion

Relationships between ϵ'' at 100 kHz and temperature for the untreated and treated samples were shown in Fig. 1. The relaxation due to methylol groups was observed around -30°C at 100 kHz for the untreated sample. The same relaxation was also observed for the samples treated at 200, 250°C and 270°C. The maximum loss (ϵ''_m) of the treated sample treated at 200°C was comparable to that of the untreated sample. However, ϵ''_m of the samples treated above 200°C decreased with increasing *T*_{HT} and the peak of ϵ'' disappeared in the samples treated above 300°C. The temperature corresponding to ϵ''_m slightly moved to a higher temperature range with increasing *T*_{HT}. On the other hand, another relaxation with very large magnitude was observed in the different temperature and frequency location for the samples treated at 500°C and 600°C. The relaxation was speculated to be due to the interfacial polarization (Maxwell-Wagner type relaxation) and the results are to be reported in the following paper.

If $\epsilon'' - \log f$ curve can be expressed by the following secant hyperbolic equation⁵⁾, the relaxation magnitude ($\epsilon_0 - \epsilon_\infty$) can be calculated by $2\epsilon''_m/\alpha$ ⁶⁾.

$$\epsilon'' = \epsilon''_m \operatorname{sech} [2.303 \cdot \alpha \log (f/f_m)],$$

where ϵ''_m is the maximum value of ϵ'' , f_m is the frequency corresponding to ϵ''_m and α is a parameter which measures the width of the distribution of relaxation times. Since ϵ_0

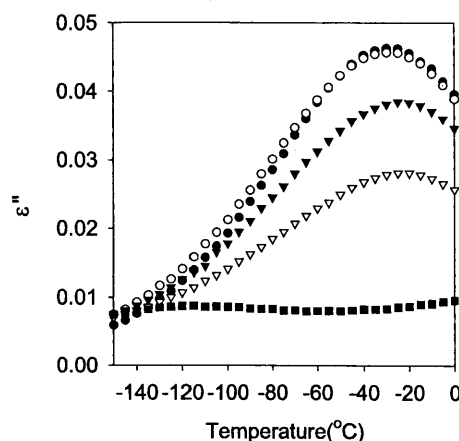


Fig. 1. Relationships between dielectric loss ϵ'' at 100 kHz for the untreated and heat treated wood powders. ●: untreated, ○: 200°C, ▼: 250°C, ▽: 270°C, ■: 300°C.

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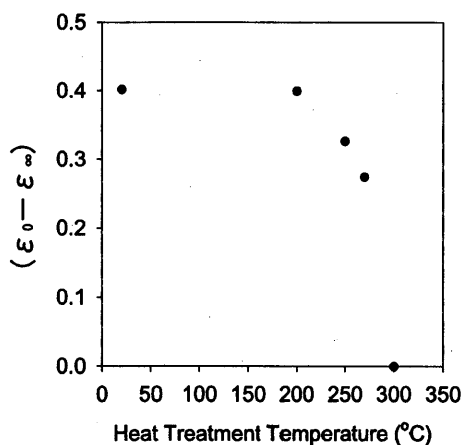


Fig. 2. Relationships between relaxation magnitude ($\epsilon_0 - \epsilon_\infty$) due to the motions of methylol groups and heat treatment temperature for wood powders.

is the static dielectric constant and ϵ_∞ is the dielectric constant at very high frequencies at which the orientation of any dipoles is impossible, ($\epsilon_0 - \epsilon_\infty$) shows an increment of dielectric constant due to the orientation polarization of dipoles, in other words the concentration of dipoles existing

in the sample. If a linear relationship between $\cosh^{-1}(\epsilon''_m/\epsilon'')$ and $\log(f/f_m)$ was obtained, $\epsilon'' - \log f$ curve can be expressed by above secant hyperbolic equation. The value of α is determined from the slope of the linear equation and ($\epsilon_0 - \epsilon_\infty$) is calculated. When experimental values of $\cosh^{-1}(\epsilon''_m/\epsilon'')$ for the untreated and treated samples were plotted against $\log(f/f_m)$, the linear relationships were recognized. The value of α at -40°C for the untreated sample was 0.23, indicating a very wide distribution of relaxation times. The value remained unchanged up to 250°C , but decreased to 0.20 at 270°C and to 0 at 300°C . Fig. 2 shows the relationship between ($\epsilon_0 - \epsilon_\infty$) and T_{HT} at -40°C . The value of ($\epsilon_0 - \epsilon_\infty$) decreased abruptly from 200°C and reached 0 at 300°C .

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